

# Recovery of Crystalline Magnesium Chloride-Hexahydrate by Solar Evaporation of Sea Bitterns

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## ABSTRACT

*Bitterns available from the solar salt industry contain about 50 parts per thousand of magnesium ion, which separates out in the form of bischofite ( $MgCl_2 \cdot 6H_2O$ ) and carnallite ( $KCl \cdot MgCl_2 \cdot 6H_2O$ ). Because bischofite is a highly hygroscopic salt, its recovery by solar evaporation of bitterns is restricted by conditions of atmospheric relative humidity. Its collection is further limited by the temperature of the mother liquor. Studies were carried out to*

*find these limiting values of the relative humidity and the temperature of mother liquor. The work indicates that such a critical value of relative humidity is limited to 55 per cent and that of temperature of mother liquor to  $43.5^\circ C$ . Such conditions are available in arid and semi-arid regions in the early part of the day. A method of collection of magnesium chloride-hexahydrate under such conditions is described.*

## INTRODUCTION

The major elements found in seawater are chlorine (55.06%), sodium (30.6%), oxygen (5.5%), magnesium (3.7%), sulphur (2.564%), calcium (1.175%), potassium (1.1%) and bromine (0.186%). Magnesium is the fourth most abundant element dissolved in seawater, and in terms of total value currently extracted, it is second only to sodium chloride.

Magnesium is abundantly present in seawater evaporites as chloride (9.44%), sulphate (6.5%) and bromide (0.22%). The raw material of the magnesium industry is, however, magnesium hydroxide. This is then treated with hydrochloric acid to obtain magnesium chloride. The potential value of magnesium chloride as a raw material is established, but it involves separation of different salts to obtain magnesium chloride in a relatively pure form. In the electrolytic process to obtain magnesium metal, sulphate and boron impurities in magnesium chloride are required to be kept at minimum, as these impurities affect the electrodes.

Magnesium chloride occurs in nature as bischofite ( $MgCl_2 \cdot 6H_2O$ ) and as carnallite ( $KCl \cdot MgCl_2 \cdot 6H_2O$ ), both of which are of oceanic origin.

In the solar evaporation of seawater to obtain sodium chloride, the end liquor left over at the sp. gr. 1.26 is evaporated to obtain carnallite ( $KCl \cdot MgCl_2 \cdot 6H_2O$ ) between sp. gr. 1.29 and sp. gr. 1.33. The carnallite contains only about 34.4% of magnesium chloride; hence it cannot be

used economically as a source of magnesium chloride. On progressive evaporation of this bittern between sp. gr. 1.33 and sp. gr. 1.37 magnesium chloride predominantly precipitates in the form of magnesium chloride hexahydrate. Further concentration by solar evaporation beyond this specific gravity does not become possible due to the high viscosity of the liquid and absorption of moisture from the atmosphere.

## EARLIER WORK

Earlier work carried out by Chaudhari (1965) for the production of crystalline magnesium chloride hexahydrate by solar evaporation of low-sulphate-containing inland bittern has yielded a product suitable for electrolytic production of magnesium metal. Utilization of a sea bittern for the production of such crystalline magnesium chloride hexahydrate has not been attempted, probably due to higher value of sulphate content of about 3.5 per cent at sp. gr. 1.350.

## EXPERIMENTAL

Tray experiments conducted to study the separation of different solid phases during solar evaporation of sea bitterns lend support for recovery of magnesium chloride hexahydrate under field conditions.

The analysis of a sample of precipitate separating out between sp. gr. 1.347 and sp. gr. 1.377 obtained by solar evaporation of bitterns is given in Table 1.

TABLE 1

Analysis of Salts Separating from Sea Bittern on Solar Evaporation in the Laboratory Experiment

NaCl	..	2.4
KCl	..	0.24
MgBr <sub>2</sub>	..	0.61
MgCl <sub>2</sub>	..	41.63
MgSO <sub>4</sub>	..	5.33

The results indicate that this fraction contains predominantly magnesium chloride viz. 41.63%.

The experimental solar evaporation of sea bittern was conducted in a tray having 1800 cm<sup>2</sup> area during the period when atmospheric relative humidity was varying between 32% and 73% but did not exceed 55% for the greater part of the experimental period.

The field trials to obtain crystalline magnesium chloride hexahydrate were conducted in a crystallizer covering an area of 300 square metres. Sea bitterns progressively concentrated by solar evaporation to sp. gr. 1.350 were fed to this crystallizer. The depth of the bitterns was maintained at 15 cm. Evaporation was continued till the density increased to sp. gr. 1.370/1.377. In this concentration range a mass of feather-like needle-shaped crystals of magnesium chloride-hexahydrate separated and was found floating at and immediately below the surface of the bitterns. The product was drawn together by means of a wooden scraper and collected in clean cane baskets daily in the cool morning hours. The product was further centrifuged to remove adhering mother liquor. The temperature of bitterns during the period of collection varied in the range of 38°C to 43.5°C, while the atmospheric temperature indicated a diurnal variation between 42°C and 16°C.

The crystals of magnesium chloride hexahydrate showed a tendency to gradually pass into solution in the mother liquor beyond 44°C till the temperature rose to 50°C when the entire mass dissolved. The field trials were carried out in two successive years, each time collecting a quantity of 150 Kg and 500 Kg respectively. The analysis of the product is presented in Table 2. The sample of precipitate that deposited on the bed of the crystallizer was also drawn and

TABLE 2

Analysis of Magnesium Chloride Hexahydrate, Percentage on Dry Basis

1) Matter Insoluble in Water	N.A.
2) Sulphate as SO <sub>4</sub> , percent (max)	0.22
3) Iron as Fe, percent (max)	N.A.
4) Boron as ppm	20
5) NaCl	0.21
6) MgCl <sub>2</sub> ·6H <sub>2</sub> O percent (min)	97.8
MgCl <sub>2</sub> (45.92%)	
7) Free and Bound Water	53.54

analysed. The product essentially contained magnesium sulphate monohydrate. The analytical result is presented in Table 3.

## RESULTS AND DISCUSSIONS

The relative humidity conditions otherwise detrimental for solar evaporation of bitterns are influenced by high temperatures during the day time and considerably lower temperatures during the night period which prevail in the arid and semi-arid tropical regions. Such conditions favour separation of the magnesium chloride hexahydrate from the supersaturated liquid during the cooler part of the night.

In this separation of magnesium chloride hexahydrate, however, kieserite (magnesium sulphate monohydrate) precipitates simultaneously. It settles on the bottom of the crystallizer. This is observed from analysis of the precipitate crust collected from the bottom. This is explained by the fact that the kieserite is a denser material than that of bischofite crystals, which have a low bulk density and, therefore, remain suspended in the liquid.

The relative humidity of the atmosphere varies over the daily evaporation cycle, touching a minimum value during the hotter part of the day. Bittern containing more hygroscopic salt of magnesium chloride hexahydrate evaporates during the dry part of the day and reabsorbs moisture with the increase in humidity (Chaudhari, 1968). The absorption of moisture in such a still body of liquid is confined to the surface layer only. Hence the dilution effect, due to diffusion being a slow process, is negligible. Thus the separation of magnesium chloride hexahydrate from the supersaturated bittern occurs during the night upon cooling and is very little affected because of the dilution effect.

## CONCLUSIONS

The absorption of atmospheric moisture by a solid substance is indicative of its critical relative humidity. The critical relative humidity of bischofite is 33.0% at 25°C (Stokes and Robinson, 1949). Hence it is seen that in the arid and semi-arid tropical regions, solar evaporation of sea bittern reaches the equilibrium density of sp. gr. 1.377 as at equilibrium relative humidity of 32% (Derby and

TABLE 3

Analysis of the Crust Settled at the Bottom of Crystallizer

	Percentage on Air Dry Basis
1) Magnesium Chloride	4.98
2) Magnesium Sulphate	45.93
3) Sodium Chloride	9.12
4) Potassium Chloride	7.32
5) Insolubles	0.16
6) Free and Bound Moisture	32.49

Ingar, 1916). This clearly approaches the equilibrium of the pure system of magnesium chloride hexahydrate and water enabling one to take advantage of solar evaporation in the process.

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